

PATENT SPECIFICATION

(11) 1 509 797

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(21) Application No. 17047/75 (22) Filed 24 April 1975

(44) Complete Specification published 4 May 1978

(51) INT CL² B32B 1/00; C11D 3/395//D06L 3/06

(52) Index at acceptance

B2E 199 200 288 327 410 417 438 439 498 53X 570 580 620
626 708 742

C5D 6A5C 6A5D1 6A5D2 6A5E 6B10A 6B12B1 6B12E
6B12N1 6B6 6B7 6B9 6C6

D1P 1A1A7 1A3 1A5 1C1A 1C4

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(54) ENCAPSULATION PROCESS

(71) We, UNILEVER LIMITED, a company organised under the laws of Great Britain, of Unilever House, Blackfriars, London E.C.4, England, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a particulate organic chlorine bleaching agent having a coating of a special type.

In the detergent bleach field particulate organic chlorine bleaching agents, such as potassium dichloroisocyanurate, sodium dichloroisocyanurate, and the hydrates thereof are employed in home laundering operations as dry bleach products to be added separately to a washing machine or for use in admixture with particles of a detergent composition to form a commercially acceptable detergent — dry bleach combination. Because of their highly reactive nature the particles must not only be thoroughly and imperviously coated to avoid contact of the bleach particles with the detergent particles, but the coated particles must not attack textile materials or the dyes thereon under washing conditions. Although prior-art processes may provide thorough and uniform coatings, the coated particles suffer the defect that they can attack fabric causing 'pinholing'.

Pinholing is caused by solid particles of an organic chlorine bleaching agent being able, through incomplete dissolution in the washing liquor, to come into physical contact with fabric.

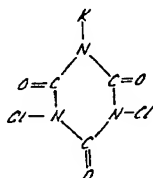
Thus the problem which it is necessary to solve in order successfully to coat an organic chlorine bleaching agent is this: that the coatings which are most satisfactory from the point of view of protecting the bleaching agent from atmospheric attack are also the ones which result in reduced bleaching performance, either because they do not release the bleaching agent at all, or because they release it too slowly (which leads to low available chlorine in the washing liquor), or because they release it too quickly producing pinholing.

We have now discovered that the above problems can be mitigated by the use of a double coating consisting of an inner fatty acid layer covered with a layer of a water soluble salt thereof.

Accordingly, the present invention provides particles of an organic chlorine bleaching agent having a double coating comprising an inner layer consisting predominantly of a fatty acid having a melting point above about 105°F and an outer layer consisting predominantly of a water-soluble salt thereof.

The present invention is described here using potassium dichloroisocyanurate as an example.

Potassium dichloroisocyanurate, typical of the cyanurates suitable as chlorine bleaching agents, is commercially available and may be obtained from the Monsanto Chemical Company. The chemical structure of this compound may be represented by the graphic formula:



Information regarding this and three related compounds may be found in Monsanto Technical Bulletin I—177.

However any particulate organic chlorine bleaching agent may be used, although mono-, di- or trichloroisocyanurates are preferred.

Among the organic chlorine bleaching agents suitable for coating are potassium dichloroisocyanurate, sodium dichloroisocyanurate, monochloramine, dichloramine, nitrogen trichloride, [(mono-trichloro)-tetra-(mono-potassium dichloro)] penta-isocyanurate, 1,3-dichloro-5,5-dimethyl hydantoin, paratoluene sulfondichloroamide, trichloromelamine, N-chloroammeline, N-chloro-succinimide, N,N'-dichloroazodicarbonamide, N-chloro acetyl urea, N,N'-dichlorobiuret, chlorinated dicyandiamide, trichlorocyanuric acid, and dichloroglycoluril.

The present invention is applicable to particulate substances having a wide range of particle sizes, so long as the particles are fluidizable. Preferably, particles having an average diameter of from 1.2 to 1.6 mm are used.

A solvent will be used for applying the fatty acid coating, substance to the particles and this will be selected with due regard for its volatility and inertness toward the core material. Preferably the boiling point of the solvent will be about 90°F to about 180°F. The dissolving capacity of the solvent will be considered in determining whether a solvent having a boiling point in the upper portion of the foregoing range can be used. For example, if relatively little solvent is required for the coating substance, the boiling point can be higher than in instances wherein a high proportion of solvent is needed.

In the double coating in accordance with the invention, it is essential that the first coating be a saturated fatty (alkanoic) acid which is solidifiable and which remains solid at temperatures likely to be encountered during manufacture or storage, for example, a temperature of at least about 105°F. Suitable fatty acids are the well-known n-alkanoic acids having from 12 to 20 carbon atoms. A particularly suitable fatty acid is Emersol 132 (Registered Trademark of Emery Industries, Inc.), which is substantially 45% stearic acid and 55% palmitic acid and which melts at about 131°—132°F. The fatty acid is applied as a solution in a suitable solvent, methylene chloride being preferred because of its compatibility, non-reactivity with chlorine bleaching agents, nonflammability, and low toxicity.

Moreover, the fatty acid will be selected with due regard to its melting point in relation to the use to which the coated particles are to be put. For example, in the case of a double-coated product intended for use as a bleaching agent in a home laundering operation, the melting point of the fatty acid may be somewhat higher than the temperature of the wash solution, but not so high that it is not removed from the core by the emulsifying action of the outer soap layer.

The following fatty acids or mixtures thereof are suitable.

	Number of Carbon Atoms	Approximate Melting Point, 0°F
Lauric Acid	12	111
Myristic Acid	14	136
Palmitic Acid	16	147
Stearic Acid	18	157
Arachidic Acid	20	169

Specific mixtures of saturated fatty acids suitable for use in the practice of the invention are set forth in the following list.

	Technical Designation	Typical Chain-Length Distribution Percent						Approximate Melting Point °F	
		C ₁₀	C ₁₂	C ₁₄	C ₁₆	C ₁₈	C ₂₀		
	90% lauric	4	91	4	1			104	
5	95% lauric	1	95	4				109	5
	99% lauric	0.3	99	0.7				111	
	95% myristic		2	95	3			127	
	90% palmitic			1	92	7		140	
	95% stearic				0.5	97	2.5	154	
10	Triple-pressed stearic			2	52	46		131	10
	Palmitic-stearic			8	75	17		131	
	Stearic			5	30	65		139	

The second coating is a water-soluble salt, for example a sodium, potassium, ammonium or calcium salt of the fatty acid which comprises the first coating.

When carrying out the process of the present invention, the first coating is conveniently applied by means of the apparatus shown schematically in the Figure. Referring to the drawing, reference character 1 indicates a chamber or cylindrical tower, wherein the coating or encapsulation of the particles is accomplished. At the base of tower 1 is a supporting screen 2. The tower is fitted with a manifold inlet for the tangential introduction of air shown at 4. Shown at 3 is an unexpanded bed of the particles to be coated. A downwardly projecting nozzle constituting a spraying means 5 is disposed within the tower 1.

The coating solution is contained in vessel 6 and is fed to nozzle 5 by pump 7. The spraying of the coating solution from nozzle 5 is aided by pressurized air entering tower 1 at 8. Fluidizing gas passes through duct 9 and is forced through the screen support by blower 10 and is either cooled by cooling system 13, or heated by heat exchanger 11, if required, in order to maintain the fluidizing gas within a critical temperature range. An exhaust blower 12 removes solvent vapors.

The fluidizing air velocity is controlled at an optimum for good fluidization. Too low a velocity will result in poor particle circulation and hence a poor coating. Too high a velocity will promote mechanical breakdown of the particles and excessive particle carryover from the body of the bed.

The temperature of the fluidizing air, and hence the temperature of the bed, is controlled within a critical range. Too low a temperature results in too low a rate of solvent evaporation causing the particles to become too wet, circulate poorly, and agglomerate. Too high a temperature tends to evaporate the solvent prematurely before the coating solution contacts the particle to be coated. Normally the temperature of the fluidizing air is such that the bed temperature is about 80°F to about 130°F.

Particles coated by the above-described procedure are substantially completely covered with a continuous coating, and are free-flowing and non-agglomerated.

It is important that each bleaching agent particle be fully covered before the subsequent treatment providing the fatty acid soft layer, since this is effected by treatment with an alkali hydroxide, and contact thereof with a chlorinated compound may result in a violent reaction.

After removing the fatty acid-coated particles from the fluidizer, the particles are treated to provide an outer coating of the water-soluble salt of the fatty acid which comprises the first coat. The outer coating is advantageously provided by gently agitating the fatty acid coated particles in for example an aqueous solution of an alkali metal or alkaline earth hydroxide having a concentration as set forth hereinafter, for about 10 minutes to about 2 hours, preferably for about $\frac{1}{2}$ hour, and until the hydroxide reacts with a portion of the fatty acid, and completely coats the

particles with the reaction product of the fatty acid and the hydroxide.

The temperature of the hydroxide solution is suitably between about 35°F and about 200°F and is not higher than the melting point, and preferably not higher than about 5°F below the melting point, of the particular fatty acid employed for the first coat, and in any event not sufficiently high to melt the fatty acid.

Following the aforementioned treatment the double coated particles are separated from the treating solution for example by decantation on a screen, and dried to produce completely coated, free-flowing, particles coated with a first or inner layer of fatty acid, and a second or outer layer of the fixed alkali soap of the fatty acid.

When the alkali is sodium hydroxide its concentration should be between about 3% to about 10% by weight when the primary coating is stearic acid or a mixture of stearic and palmitic acids, and should be about 10% to about 15% when the primary coating is lauric acid or the commercial 95% pure material. The concentration of potassium hydroxide should be between about 10% and about 15%. Calcium hydroxide should be applied as a saturated solution, i.e., about 0.1% by weight.

Coated particles of organic chlorine bleaching agent prepared in accordance with the instant invention find utility in admixture with particulate detergent compositions having therein and anionic or nonionic detergent species that is not adversely affected by chlorine liberated from the bleaching agent.

Suitable anionic detergents are primary and secondary alkyl sulphates, such as sodium and potassium lauryl sulphate, alkyl benzene sulphonates such as sodium dodecylbenzene sulphonate and soaps.

Suitable nonionic detergents are the ethylene and propylene oxide condensates of primary and secondary aliphatic alcohols and mixtures thereof having about 8 to about 16 carbon atoms in the alcohol chain, the proportion of ethylene and propylene oxide being from about 50 to 80% by weight of the material. Similar condensates of alkylphenols are also suitable.

Further details of these conventional detergent ingredients can be obtained from standard text books and from manufacturers' trade literature.

Preferably the detergent composition should be substantially free of compounds containing amino nitrogen to avoid adverse effects during the washing operation.

The compositions containing coated bleaching agents may be formulated with a detergent builder as a detergency aid, for example those mentioned hereinafter, to provide a commercially valuable detergent-bleach composition.

Suitable builder compounds are tetrasodium and tetrapotassium pyrophosphate, pentasodium and pentapotassium tripolyphosphate, sodium or potassium carbonate, sodium or potassium silicates having an $\text{SiO}_2:\text{Na}_2\text{O}$ ratio of about 1:1 to about 3.2:1, hydrated or anhydrous borax, sodium or potassium sesquicarbonate, and polyphosphonates such as sodium or potassium ethane-1-hydroxy-1, 1-diphosphonate.

Also useful are the organic detergent builders which have been proposed recently in order to reduce the level of phosphate in detergents. These include sodium or potassium oxydisuccinates, carboxymethyloxysuccinates, and ester-linked carboxylate derivatives of polysaccharides, such as the sodium and potassium starch maleates, starch and oxidized heteropolymeric polysaccharides.

The weight percent of the builder present in the built anionic detergent composition is from an amount of about 6% and up to about 90% and preferably from about 20% to about 60%. Suitably, a builder may be present in the ratios of about 0.5 to about 10 parts by weight, preferably about 2 to about 5 parts by weight, for each part by weight of the detergent component.

Other conventional materials may be present in the detergent compositions of the invention. Typical examples include the well-known soil suspending agents, corrosion inhibitors, dyes, perfumes, fillers, optical brighteners, enzymes, germicides and anti-tarnishing agents. The balance of the detergent composition may be water.

Detergent compositions formulated for use in the washing of fabrics in automatic washing machines may contain about 5% to about 30% anionic detergent, about 30% to about 60% of one or more of the builders mentioned hereinabove, and sufficient coated bleaching agent to provide 30—200 parts per million chlorine in the wash water, or approximately 2% to 25% of the agent in the detergent formulation. Usually included are about 0.1—0.3% optical brightener, and about 0.4% sodium sulfate, and if desired small proportions of other

components such as germicides, and anti-caking agents to confer special properties on the product.

When the detergent is soap, and comprises the major proportion of the detergent-bleach product, the soap may be present in amounts from about 60% to about 90%, little or no building being required, although about 1% to about 10% of an alkaline builder may be advantageous.

When the detergent is nonionic, from about 5% to about 20% is suitable, the balance of the composition being as listed above.

Detergent compositions formulated for mechanical dishwashers and having the coated bleaching agents of the invention therein may contain low proportions of nonionic detergent, for example about 1% to about 4%, and may contain a suds depressant and a high proportion of a builder, for example about 50%—90% of a mixture of sodium tripolyphosphate, sodium carbonate, and sodium silicate.

The invention is further illustrated in the following examples, of which Example 2 illustrates application of a first coating only.

Example 1.

This example describes a process for coating potassium dichloroisocyanurate with a double coating.

Thirteen pounds of extra coarse grade potassium dichloroisocyanurate are charged onto the perforated plate of the cylindrical coating tower 1 in the Figure. The perforated plate is a 60-mesh stainless steel screen. The particles are fluidized and suspended by an upwardly moving air stream supplied by blower 10. The superficial air velocity of the fluidizing air stream is 8.5 feet per second. The temperature of the air is maintained at $95^{\circ} \pm 2^{\circ}\text{F}$, by heat exchanger 11.

The primary coating solution is prepared by dissolving triple-pressed stearic acid (about 45% stearic acid) in methylene chloride to form a 20% solution. A small amount of ultramarine blue is dissolved in the coating solution for subsequent use in observing the continuity of the primary coating.

The primary coating solution is sprayed on the fluidized particles 3, through nozzle 5, appropriately adjusted as to height. Nozzle 5 has six orifices disposed to provide a diverging spray pattern. An auxiliary stream of air is applied to the fluidized bed through 9 nozzles horizontally disposed at the perforated support screen level with the tips of the nozzles placed close to the inner wall of the tower. The air leaves these nozzles in a horizontal path substantially tangential to the wall of the tower. It is the function of this tangential air to assist in keeping in motion the particles at the outer periphery of the plate which do not obtain the full effect of the fluidizing air.

The coating solution is applied to the fluidized particles for a period of 2 hours. The weight of the coating is about equal to the weight of the original particles. The coated particles are of uniform blue color and size, with substantially no agglomeration, and are dry and free-flowing. When some of the coated particles are left immersed for 2 days in an acidified potassium iodide solution, no color change is observed, indicating complete encapsulation of the particles.

The second coating is applied in the following manner.

A 5.2% sodium hydroxide solution is prepared by diluting 60 grams of 50% NaOH solution with 520 grams of distilled water in a two-litre beaker. The dilute solution is heated to 110°F in a water bath and 200 grams of the particles coated as described above are placed in the NaOH solution and gently agitated for 30 minutes, maintaining the temperature of the solution between 105°F and 110°F . The molar ratio of NaOH to fatty acid is 2:1. After the 30 minute treatment, the solution is decanted through a 25-mesh stainless steel screen, and the particles on the screen are dried at room temperature for 24 hours. The particles are free flowing and white, indicating complete covering of the blue-colored first coat.

The single- and double-coated particles are tested for ease of chlorine release and for adverse effect on cloth in the following manner

Six pounds of white cotton fabric are placed in a top-loading automatic washing machine. Three swatches of blue denim cloth and one swatch of black 65/35 Dacron*/cotton cloth (* 'DACRON' is a Registered Trade Mark) each measuring 12×12 inches are placed on top of the cotton cloth in circular configuration. Next, there is placed directly on the fabric 3.4 ounces of a detergent-bleach composition containing 8.0% of the coated material prepared as above. Water at a temperature of $132^{\circ}\text{F} \pm 3^{\circ}\text{F}$ is run directly on the detergent-bleach composition for about 150 seconds to a volume of 17.4 gallons. The wash

solution is agitated for 10 minutes, and the fabrics are examined. The results are shown in Table 1.

TABLE 1.

Bleach Composition *KDC Coated With	% Available Chlorine	Pinholing (Blue Denim)	% Chlorine Released
Single Coat with Fatty Acid			
Fatty Acid (A)	35.0	3	97—100
Fatty Acid (B)	37.5	0	20
Fatty Acid (C)	39.0	1	41.5
Dual Coat — First Coat = Fatty Acid (A)			
2.85% NaOH 10 min.	21.03	2	not determined
5.34% NaOH 30 min.	23.19	1	69.83
10.33% NaOH 30 min.	26.15	1	87.70
(A) about 45% stearic acid and 55% palmitic acid; m.p. 131—132°F			
(B) 95% palmitic, 4% stearic, 1% myristic acids; m.p. 138—144°F			
(C) about 70% stearic acid and 30% palmitic acid; m.p. 138.5—143°F.			
Pinholing Rating			
0 = non (excellent)			
1 = minimal pinholing (acceptable)			
2 = severe pinholing (unacceptable)			
3 = very severe pinholing (unacceptable)			
* Potassium dichloroisocyanurate			

5 From the foregoing data in Table 1, it may be seen that a single coating of fatty acid is inadequate to accomplish the dual purpose of providing a high chlorine release and at the same time avoid pinholing. It will be noted that fatty acid (A) having a melting point below the temperature of the wash water, melts to release all of the chlorine in the coated bleaching agent but causes pinholing, due to contact with the fabric upon the melting of the fatty acid coating. Fatty acids 10 (B) and (C), having melting points above the temperature of the wash water, are unsatisfactory, since they do not allow a sufficient release of chlorine to be of any value as a bleach, although the low level of chlorine release prevents pinholing. Again referring to the foregoing data, it will be observed that a double coating 15 applied in accordance with the invention prevents pinholing to a substantial extent, and additionally allows an adequate release of chlorine. 15

Example 2.

This example further illustrates the present process for applying a first coating of fatty acid to particles of potassium dichloroisocyanurate.

20 A coating solution is prepared in vessel 6 in the Figure by dissolving 10 pounds of fatty acid (about 70% stearic acid and 30% palmitic acid) in 40 pounds of methylene chloride. Twenty grams of blue pigment is added and the solution warmed at 95°F. 20

25 Ten pounds of extra coarse grade potassium dichloroisocyanurate is screened to 25 mesh and placed on the 40-mesh supporting screen in coating tower 1. Fluidizing air is forced into the apparatus through duct 9 at a superficial air 25

velocity of 6.8 feet per second. Tangential air is supplied as needed. The temperature of the bed is maintained at $107 \pm 2^\circ\text{F}$.

5 The coating solution is sprayed downward onto the fluidized bed through a 6-hole atomizing nozzle located 12 inches above the supporting screen. The coating is applied at the rate of 6.7 pounds per hour, and the solvent is evaporated at the rate of 23 pounds per hour. 5

10 The coated product is a dry, nonagglomerated, free-flowing particulate solid of which the particles are substantially uniform in size. A test in potassium iodide solution indicates that the particles are completely covered. 10

After storing for 8 weeks at 80°F and 80% relative humidity admixed with particles of a commercial detergent, substantially no loss of chlorine occurs. In a control experiment in which the potassium dichloroisocyanurate is uncoated, it loses 90% of its chlorine.

Example 3.

15 A spray-dried detergent composition having the following formula is prepared by conventional procedures. 15

	% Alkylbenzenesulfonate	10.0	
	% Sodium tripolyphosphate	33.0	
	% Sodium silicate solids ($\text{SiO}_2:\text{Na}_2\text{O} = 2.4$)	6.0	
20	% Optical brightener	0.1	20
	% Carboxymethylcellulose	0.3	
	% Water	10.0	
	% Sodium sulfate and miscellaneous matter introduced with the components	40.0	
		<u>100.0</u>	

25 To separate portions of the above-described compositions are mixed various proportions of the product of Example 1, the proportions being as follows. 25

Example No.	Parts by Weight					
	3A	3B	3C	3D	3E	
Spray-dried composition	80	84	88	92	96	
30 Product of Example 1	20	16	12	8	4	30

Example 4.

A composition suitable for use in mechanical dishwashers and having the following formula is prepared by conventional techniques.

	% Nonionic detergent ^(a)	2.0	
35	% Sodium tripolyphosphate	20.0	35
	% Trisodium orthophosphate	25.0	
	% Sodium metasilicate	13.0	
	% Water	10.0	
40	% Double coated organic chlorine bleaching agent having an inner coating of fatty acid and an outer coating of water soluble salt thereof	30.0	40
		<u>100.0</u>	

- (a) A condensate of a mixture of primary aliphatic alcohols having about 12—15 carbon atoms with about 25% lower alkyl branching on the 2-carbon, and about 9 molar proportions of ethylene oxide.

Example 5.

5 This example shows the effect on stability of coated and uncoated chlorinated cyanates admixed with a detergent composition when stored variously in open wax-laminated barrier cartons and in open and closed non-barrier cartons, i.e., allowing free or only partially restricted passage of vapors.

10 Mixtures are prepared, stored and analyzed as follows.
Eight parts by weight of the double coated potassium dichloroisocyanurate prepared as described in Example 1 are admixed with 92 parts by weight of a spray-dried detergent composition having the formula set out in Example 3 and divided to produce 3 equal batches of material (a—c). Two similarly sized batches of uncoated potassium dichloroisocyanurate (e and f) and one of potassium dichloroisocyanurate dihydrate (d) were also prepared. The batches were stored.

15 After 2 weeks' storage at 80°F and 80% relative humidity, the chlorine losses are determined. The protective action of the double coating as compared with uncoated particles of chlorine bleaching agent is evident from the data set forth below:

Example	Storage Time	
	0 Week	2 Weeks
5a % Chlorine % Loss	2.31 —	2.26 2.1
25 5b % Chlorine % Loss	2.28 —	2.21 3.1
5c % Chlorine % Loss	2.29 —	2.28 0.4
5d % Chlorine % Loss	2.09 —	0.96 54.1
30 5e % Chlorine % Loss	2.08 —	1.75 15.9
5f % Chlorine % Loss	1.99 —	1.86 6.5

WHAT WE CLAIM IS:—

- 35 1. Particles of an organic chlorine bleaching agent having a double coating comprising, an inner layer consisting predominantly of a fatty acid having a melting point above about 105°F and an outer layer consisting predominantly of a water-soluble salt thereof.
- 40 2. Particles as claimed in claim 1 wherein the chlorine bleaching agent is a mono-, di- or tri-chloroisocyanurate.
3. Particles as claimed in claim 2 wherein the chlorine bleaching agent is sodium or potassium trichloroisocyanurate.
4. Particles as claimed in any one of the preceding claims wherein the particles before coating have an average particle diameter of from 1.2 to 1.66 mm.
- 45 5. Particles as claimed in any one of the preceding claims wherein the fatty acid is a C₁₂ to C₂₀ fatty acid or a mixture of such acids.
6. Particles as claimed in any one of the preceding claims wherein the fatty acid is a mixture of stearic and palmitic acids having a melting point of about 130°F.
- 50 7. Particles as claimed in any one of the preceding claims wherein the water-soluble salt of the fatty acid is a sodium or ammonium salt.
8. Particles of a chlorine bleaching agent having a coating in two layers substantially as hereinbefore described in any one of Examples 1 and 3 to 5.
9. A particulate detergent composition comprising a detergent active

compound and particles of a chlorine bleaching agent as claimed in any one of the preceding claims.

5 10. A particulate detergent composition comprising a detergent active compound and a chlorine bleaching agent having a coating in two layers, substantially as hereinbefore described in any one of Examples 1 and 3 to 5. 5

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Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1978.
Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from
which copies may be obtained.

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1 SHEET

COMPLETE SPECIFICATION
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